Simple Cu_2ZnSnS_4 recipes from ab initio thermodynamics

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Global photovoltaic (PV) electricity generation is currently of the order 7GW, while global energy consumption (including liquid fuels) is of the order 15TW. In order to make a significant contribution to the energy mixture, PV generation must be hugely expanded. Ultimately, "country-sized" schemes are needed.[1] A useful approach to raise the application of PV by orders of magnitude is building-scale functional coatings. This aligns with the interests of building cladding manufacturers, including Tata Steel and NSG, which are backing the SPECIFIC consortium to develop building-integrated technologies. Abundant thin-film absorbers such as Cu_2ZnSnS_4 (CZTS) are attractive for providing PV. However, scalable roll-to-roll processes are far-removed from laboratory prototypes.

Roll-to-roll considerations

A number of synthesis routes have been identified, but whether the precursors are binary compounds, salts in solution, metal alloys or pre-formed CZTS nanoparticles, film formation typically takes place in a high-temperature annealing process with sulfur vapour. This critical step involves complex phase equilibria and is suited to a thermodynamic study. In roll-to-roll processing, annealing must be kept as rapid as possible in order to support a continuous production line. It is also difficult to supply pressures which are far-removed from ambient.

Near-infrared (NIR) heating is of particular interest, and has already been applied to rapid sintering of TiO_2 for dye-sensitised cells.[2] Industrial partners are also keen to avoid some of the dangerous materials used to produce experimental devices, such as toxic H_2S and hydrazine (a rocket propellant!)

Pilot-scale roll-to-roll facilities at the SPECIFIC R&D site

Computational details

The University of Bath's 800-core Aquila cluster is used for structure optimisation and testing: demanding phonon calculations are carried out on national-scale facilities (The Cray systems "HECToR" and "ARCHER", via the EPSRC-funded Materials Chemistry Consortium, and the STFC's Bluegene/Q system "Blue Joule").

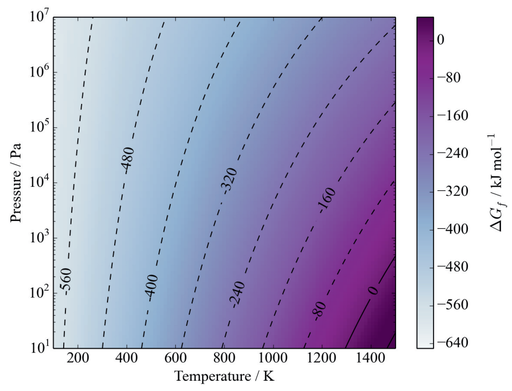
Calculations are primarily carried out using the FHI-aims quantum chemistry code with the PBEsol exchange-correlation functional. This offers a balance of efficiency and accuracy, while being readily scalable across thousands of computing cores.

Pre/post processing uses a mixture of academic pack-ages (in particular Phonopy for lattice dynamics), and Python programming.

While this aspect of the work is theoretical, the results and direction are tied to the UK-wide PVTEAM programme led in Bristol.

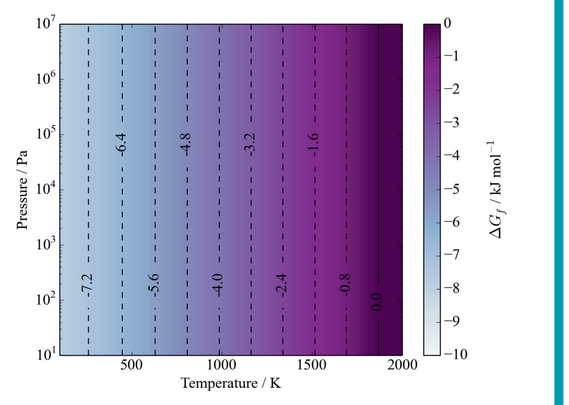
Free energy surfaces

A chief difficulty in the development of viable CZTS coatings is the complex phase diagram, which includes binary and ternary phases as well as stabililising defects.[3]



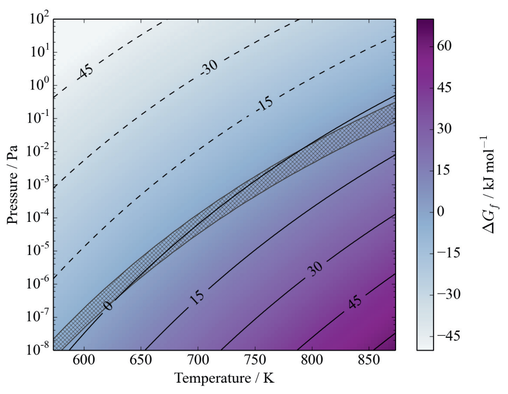
Formation free energy surface for CZTS

$2Cu + Zn + Sn + 2S_2 \rightarrow CZTS$



Free energy surface for CZTS relative to ternary

$Cu_2SnS_3 + ZnS \rightarrow CZTS$



Formation free energy surface from SnS-S system

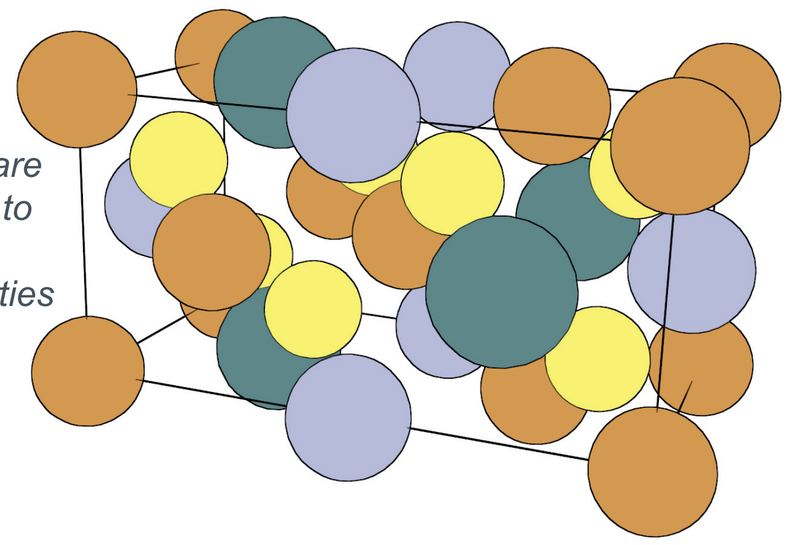
$Cu_2S + ZnS + SnS + ½S_2 \rightarrow CZTS$

Phase equilibria are explored by examining the free energy surfaces of hypothetical reactions. Once free energy data is available, interactions can be modelled rapidly. So far, the elemental components and major binary and ternary compounds have been modelled. Strong agreement has been found with experimental kinetic modelling (hashed region, left).[4,5]

Ab initio thermodynamics

The structures and energies of moderately complex crystalline materials (~100 atoms in a unit cell) may be studied with some confidence using density functional theory (DFT). These methods typically model an athermal ground state; this is not representative of typical usage conditions, and lies even further from industrial reaction conditions.

Kesterite CZTS structure from DFT calculations. Individual atoms are displaced slightly to investigate the vibrational properties of the system.



Temperature and pressure effects can be introduced by calculating key bulk properties including the heat capacity and vibrational entropy. By using harmonic vibration models to construct the chemical potential (μ) for each compound of interest, the Gibbs free energy (ΔG) may be calculated for arbitrary reactions and conditions. This determines the relative phase stability at fixed temperature and pressure.

[1] MacKay, D. J. C. *Philos Trans. R. Soc. A.* 2013, **371**, 20110431
[2] Watson, T.; Mabbett, H.; Wang, H.; Peter, L; Worsley, D. *Prog Photovoltaics* 2011, **19**, 482
[3] Chen, S.; Gong, X. G.; Walsh, A.; Wei, S. *Appl. Phys. Lett.* 2010, **96**, 021902
[4] Jackson, A. J.; Walsh, A. *J. Mater. Chem. A* 2014, **2**, 7829-7836
[5] Scragg, J. J., Ericson, T., Kubart, T., Edoff, M., Platzer-Björkman, C. *Chem. Mater.* 2011, **23**, 4625–4633

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